Tetrahedron Letters No. 49, pp 4497 - 4500, 1976. Pergamon Press. Printed in Great Britain.

THE PHOTOCHEMISTRY OF CYCLIC AND ACYCLIC NITROALKENES[1]

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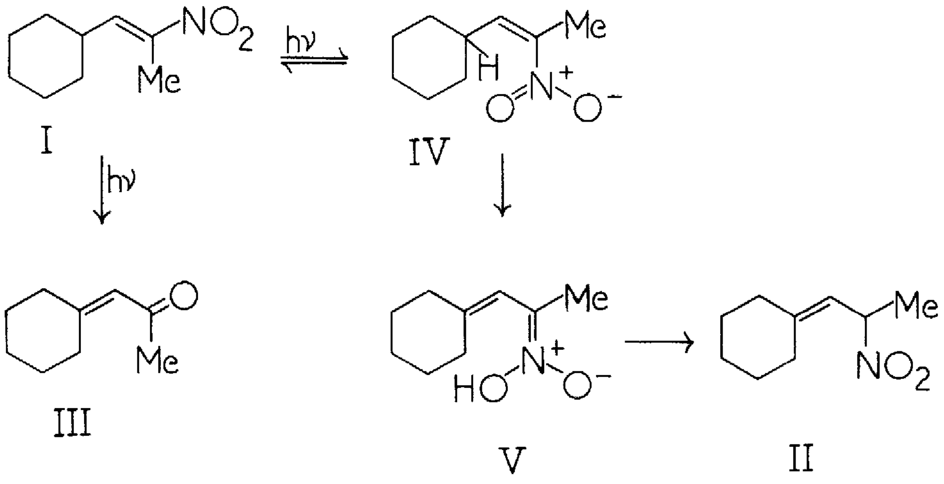
(Received in UK 8 October 1976; accepted for publication 18 October 1976)

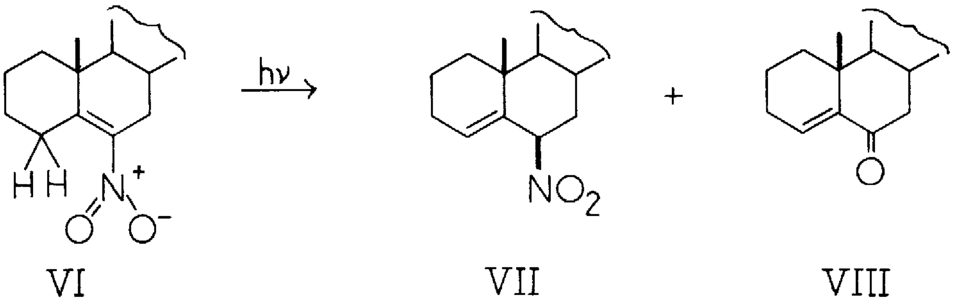
Photochemically induced rearrangements and cycloaddition reactions have been reported for 1-aryl-2-nitroalkenes, the former being typified by the rearrangement of 1-phenyl-2-nitroprop-1-ene to 1-hydroxyimino-1-phenylpropan-2-one[2] and the latter by the addition of β-nitrostyrene to alkenes.[3] The rearrangement is presumed to take place *via* an intermediate nitrite, and analogous processes have been reported for other aryl 2-nitroprop-1-enes and for 2-nitrofuran and 2-nitropyrrole.[4] A competing pathway leading to the formation of aryl aldehydes and nitrile oxides[5-7] has been observed and is believed to involve a different excited state.[7]

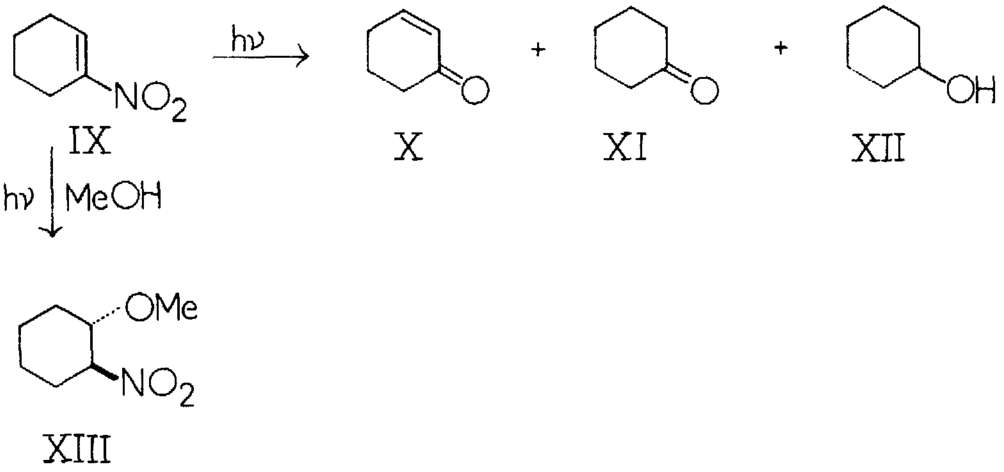
Non-aromatic conjugated nitroalkenes are less well investigated, and there have been no serious attempts to rationalise the contrasting behaviour of these systems. Double bond migration to give β,γ-unsaturated nitroalkenes in variable yield has been reported in a series of simple conjugated nitroalkenes following the establishment of a *cis, trans* equilibrium.[8] The major photoproducts of 6-nitrocholesteryl acetate are 3β-acetoxy-6β-nitrocholest-4-ene and 3β-acetoxycholest-4-en-6-one, arising respectively by double bond migration and fragmentation *via* the nitrite;[2,9,10] the study is complicated by the existence of a competing photoelimination leading to 6-nitrocholesta-3,5-diene which undergoes further photorearrangement to 3-hydroxyiminocholest-4-en-6-one. This communication reports a re-examination of the factors influencing the photochemical behaviour of conjugated nitroalkenes.

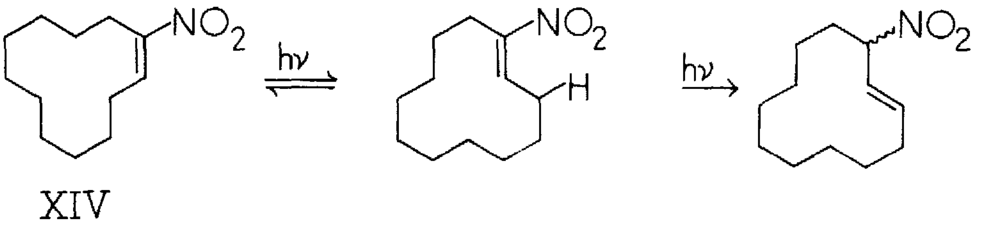
Irradiation of 1-cyclohexyl-2-nitroprop-1-ene (I) through a pyrex filter in acetone, propan-1-ol or cyclohexene gave the nitroalkene (II)[11] and cyclohexylidene acetone (III) in yields of 50-55% and 5-25% respectively. The unsaturated ketone presumably arises *via* the corresponding nitrite, a process for which there is ample precedent. The formation of the β,γ-unsaturated nitro-compound is best interpreted as involving intramolecular γ-hydrogen abstraction in the *cis*-isomer (IV), followed by rearrangement of the *aci*-nitro isomer (V) to the nitroalkene (II). An analogous pathway has been established for the deconjugation of acyclic α,β-unsaturated ketones. Support for this postulate in the case of nitroalkenes is to be found in the study of cyclic nitroalkenes. Irradiation in acetone or cyclohexane of



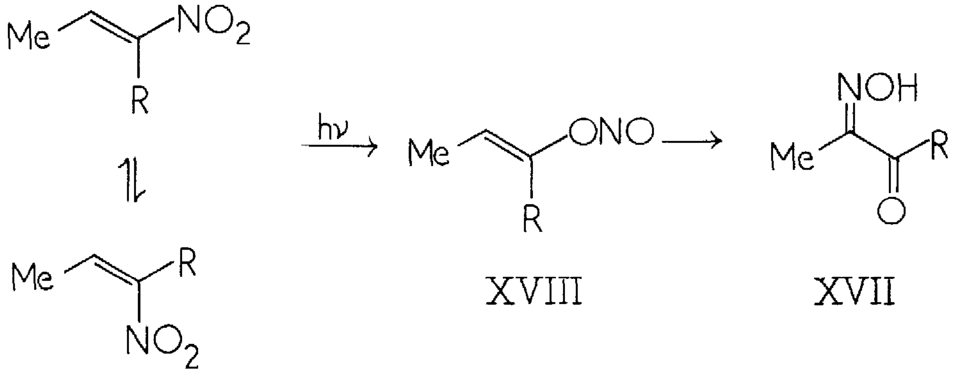
6-nitrocholest-5-ene (VI), in which a hydrogen atom is favourably positioned for abstraction *via* a six-membered transition state, affords a 45% yield of the nitroalkene (VII) together with a 20% yield of the ketone (VIII). An analogous reaction was observed in 4-nitrocholest-4-ene. Not unexpectedly, 3-nitrocholest-2-ene and 1-nitrocyclohexene (IX), which do not have γ-hydrogen atoms readily available for intramolecular abstraction, behave quite differently on irradiation. 1-Nitrocyclohexene undergoes a slow photoreaction in acetone solution leading to the formation of cyclohexenone (X), cyclohexanone (XI) and cyclohexanol (XII), whereas 3-nitrocholest-2-ene is converted into a complex mixture of products. Prolonged irradiation of 1-nitrocyclohexene in methanol affords the adduct (XIII). In neither compound is there any evidence for the formation of a β,γ-unsaturated nitro-compound. Deconjugation is observed, however, in good yield on irradiation of 1-nitrocyclododecene (XIV); in this case, relatively unstrained conformations of the *trans*-isomer exist in which the γ-hydrogen atom is in close proximity to the nitro group.







Unlike 1-aryl-2-nitroprop-1-enes, no evidence was found for the rearrangement of nitro-alkenes to oximino-ketones in this study or in previous studies of acyclic nitroalkenes.[8] A possible explanation for this observation is the known instability of some of these oximes, for example the monoxime of cyclohexane-1,2-dione, coupled with the ease of competing photo-reactions. The isolation of α,β-unsaturated ketones from many of these reactions, however, led us to believe that the nitro-nitrite rearrangement was taking place to some extent. Accordingly, a careful re-examination was made of the photochemistry of 2-nitrobut-2-ene (XV) and of 3-nitropent-2-ene (XVI), intramolecular γ-hydrogen abstraction from a primary carbon atom being less favoured. Irradiation in methanol or cyclohexane solution followed by careful tlc rather than vacuum distillation led to the isolation in yields of up to 30% of the corres-ponding oximes (XVII). This rearrangement, which presumably occurs *via* the nitrite (XVIII), is not therefore as was supposed limited to 1-aryl-2-nitroprop-1-enes, but occurs readily in non-aromatic 2-nitroprop-1-enes in which deconjugation does not compete. In 2-nitropent-2-ene in which both pathways are operative, the β,γ-unsaturated nitro-compound is obtained as the major product along with a 4% yield of the corresponding oxime.



XVIII

XVII

XV R = Me

XVI R = Et

We thank the S.R.C. for financial support and for two studentships (to P.J.M. and K.T.T.).

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11. Satisfactory analyses and spectral data have been obtained for all new compounds.